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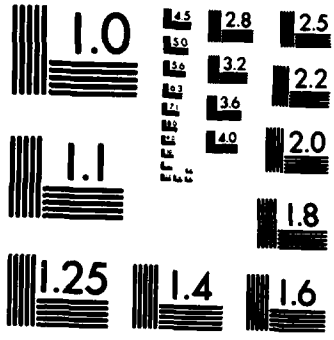

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Photoluminescent and Electroluminescent Properties of $Cd_{0.95}Mn_{0.05}Se$ Electrodes

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PHOTOLUMINESCENT AND ELECTROLUMINESCENT PROPERTIES OF $Cd_{0.95}Mn_{0.05}Se$ ELECTRODES

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Quenching of photoluminescence (PL) and initiation of electroluminescence (EL) from *n*-type $Cd_{0.95}Mn_{0.05}Se$ electrodes is used to map the electric field in these solids, grown by a modified Bridgman method.

1. INTRODUCTION

Photoluminescence (PL) and electroluminescence (EL) can be used to characterize electric fields in semiconductor electrodes through their influence on electron-hole (e^--h^+) pair recombination[1]. Solid solutions of II-VI compounds such as n-CdS and n-CdSe have provided a useful family of tunable band gap materials for such studies[2]. We have extended these studies to emissive electrodes derived from a solid solution of MnSe and CdSe. In this paper we report that PL from n-$Cd_{0.95}Mn_{0.05}Se$ electrodes used in photoelectrochemical cells (PEC's) can be used to map the electric field in these solids, and that EL obtained from the electrodes originates, on average, nearer the semiconductor-electrolyte interface than PL.

2. SYNTHESIS AND CHARACTERIZATION

Single-crystal samples of n-$Cd_{0.95}Mn_{0.05}Se$ were grown by a modified Bridgman method[3]; samples with carrier concentrations, n, ranging from ~10^{16}-10^{18} cm^{-3} (Hall method) were etched with 1:20(v/v) Br_2/MeOH prior to use. When excited with ultraband gap light (E_g 1.75eV[4]), the samples emit with λ_{max}~694nm, Fig.1. The spectral maximum is near E_g and blue-shifts to ~665nm at 77 K; radiative quantum efficiencies, ϕ_r, for the edge emission generally range from ~10^{-5} to 10^{-4}.

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3. PL PROPERTIES IN A PEC

When the solid serves as the photoanode of a PEC employing diselenide electrolyte, its PL intensity can be quenched by applied potential. Figure 1 presents photocurrent - PL intensity - voltage data (*iLV curves*) for a n-$Cd_{0.95}Mn_{0.05}Se$-based PEC; the potential-independent spectral distribution permits PL to be monitored at λ_{max}. Quenching of PL in PEC's has been described using a dead-layer model originally applied to semiconductor-metal, Schottky barrier systems: e^--h^+ pairs formed within a distance on the order of the depletion width do not contribute to PL; this model thus relates PL intensity to the thickness of the electric field in the electrode[5,6]. The quantitative form of the model is given by eq. (1), where ϕ_r and $\phi_{r_{FB}}$ are

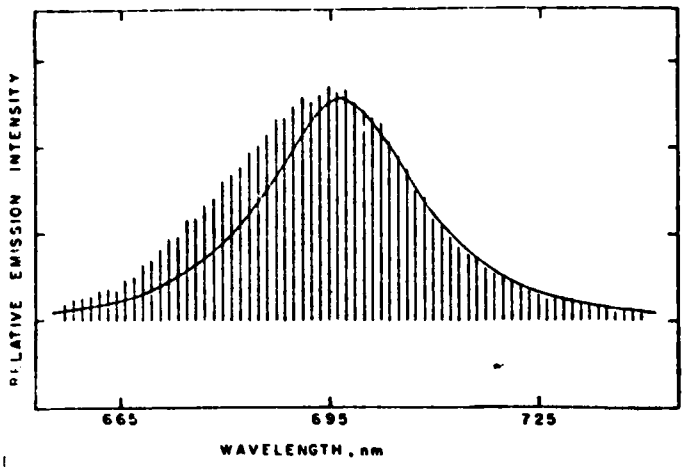
$$\frac{\phi_r}{\phi_{r_{FB}}} = \exp(-\alpha' D) \qquad (1)$$

radiative efficiencies in circuit and at flat-band potential (assumed to be open circuit), respectively; D is the dead-layer thickness; and $\alpha' = \alpha + \beta$ with α and β the solid's absorptivities for the exciting and emitted light.

Although ultraband gap absorptivities have not been measured for n-$Cd_{0.95}Mn_{0.05}Se$, values of α can be estimated by blue-shifting the CdSe absorption spectrum[7] by ~25nm, since the solids have similar electronic structures. The PL quenching resulting from a given excitation wavelength then leads, in conjunction with the estimated value of α and eq. (1), to a value for D. For the Fig. 1 data, D is calculated to be ~1200Å (α is taken to be 1.7×10^5 and $0.63 \times 10^5 cm^{-1}$ for 458 and 646nm, respectively) at -0.7V vs SCE in accord with a calculation of the depletion width. In general, good agreement of PL quenching with the dead-layer model was found and a consistent set of values for α was obtained for all samples. When the experimental curves were compared to curves calculated by assuming that all of the applied potential appears in the semiconductor[5], good accord was found, indicating that applied potential appears predominantly in the solid.

4. EL PROPERTIES

When used as a dark cathode in aqueous, $OH^-/S_2O_8^{2-}$ electrolyte, samples of n-$Cd_{0.95}Mn_{0.05}Se$ exhibit red EL. The electrode's EL spectrum, Fig. 1, is similar to its PL spectrum, but exhibits a spectral mismatch in the high-energy tail. As with n-CdS_xSe_{1-x} ($0 \leq X \leq 1$) samples, we attribute this mismatch to self-absorption effects: the enhanced intensity at short wavelengths is consistent with the origin of EL, on average, nearer the semiconductor-electrolyte interface than PL[2]. Measured EL efficiencies are ~10^{-5} to 10^{-6} [2].



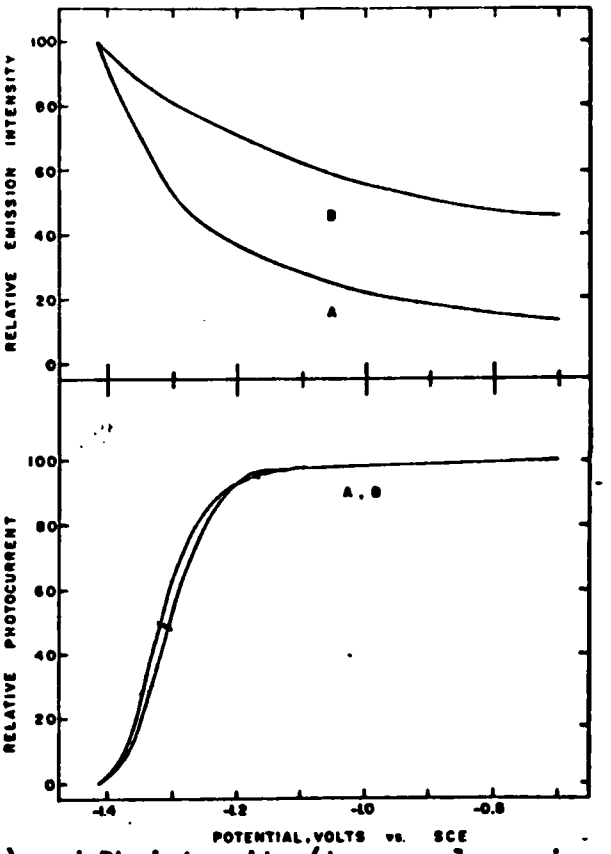


FIGURE 1

Left: Uncorrected PL (solid curve) and EL (vertical lines) spectra of n-$Cd_{0.95}$-$Mn_{0.05}Se$ obtained in the same sample geometry in $OH^-/S_2O_8^{2-}$ electrolyte (295K). The PL spectrum (632.8-nm excitation) was taken out of circuit; the EL spectrum, scaled to match the PL intensity at λ_{max}, was acquired by repetitively pulsing the electrode between 0.0 V (1.5 s) and -1.3 V vs. SCE (1.0 s)[2].

Right: Relative photocurrent (bottom panel) and PL intensity (top panel; monitored at λ_{max}) as a function of potential for an n-$Cd_{0.95}Mn_{0.05}Se$-based PEC employing diselenide electrolyte[2]. The electrode (n~4 X $10^{16}cm^{-3}$) was excited with 457.9- ("A" curves) and 646-nm ("B" curves) light in an identical geometry. PL intensities and photocurrents were arbitrarily matched at "100" at open circuit; photocurrent densities (quantum yields) at -0.7 V vs. SCE are $7mA/cm^2$ (0.7) and $3mA/cm^2$ (0.5) for curves A and B, respectively. These *i-V curves* were swept at 10mV/s.

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